



THE UNIVERSITY *of* EDINBURGH

## Edinburgh Research Explorer

### Optical activity of the super-atom molecular orbital (SAMO) states in Li@ C60+ conformers

**Citation for published version:**

Mignolet, B, Campbell, E & Remacle, F 2017, Optical activity of the super-atom molecular orbital (SAMO) states in Li@ C60+ conformers. in *AIP Conference Proceedings*. 1 edn, vol. 1906, 030027, AIP Conference Series, vol. 1906, AIP PRESS. <https://doi.org/10.1063/1.5012307>

**Digital Object Identifier (DOI):**

[10.1063/1.5012307](https://doi.org/10.1063/1.5012307)

**Link:**

[Link to publication record in Edinburgh Research Explorer](#)

**Document Version:**

Peer reviewed version

**Published In:**

AIP Conference Proceedings

**General rights**

Copyright for the publications made accessible via the Edinburgh Research Explorer is retained by the author(s) and / or other copyright owners and it is a condition of accessing these publications that users recognise and abide by the legal requirements associated with these rights.

**Take down policy**

The University of Edinburgh has made every reasonable effort to ensure that Edinburgh Research Explorer content complies with UK legislation. If you believe that the public display of this file breaches copyright please contact [openaccess@ed.ac.uk](mailto:openaccess@ed.ac.uk) providing details, and we will remove access to the work immediately and investigate your claim.



# Optical activity of The Super-Atom Molecular Orbital (SAMO) States in $\text{Li@C}_{60}^+$ Conformers

B. Mignolet<sup>a</sup>, Eleanor E. B. Campbell<sup>b</sup>, F. Remacle<sup>a</sup>

a) UR Molecular Systems, B6c, University of Liege, B4000, Liège, Belgium

b) EaStCHEM, School of Chemistry, University of Edinburgh West Mains Road, Edinburgh EH9 3FJ, Scotland

**Abstract:** Super Atom Molecular Orbitals (SAMOs) are electronic excited states found in fullerenes in which an electron is excited to one or, more generally, several virtual orbitals with hydrogen-like character. The photoexcitation mechanism of the SAMO states strongly depends on the symmetry of the fullerene. For instance the SAMOs of the spherical  $\text{C}_{60}$  fullerene are not optically active while breaking the symmetry by adding a dopant can make the SAMO states optically active. In this proceeding we investigate the optical activity of the SAMO states in several conformers of the  $\text{Li@C}_{60}^+$  fullerene and we show that the position of the lithium atom inside the fullerene cage strongly affects the computed oscillator strengths and transition dipole moments of the SAMO states.

## 1. INTRODUCTION

Fullerenes are nanostructures with a dense manifold of electronic excited states mostly composed of excitations from the HOMO or HOMO-1, to one or more often several virtual orbitals. Depending on the nature of the virtual orbital in which the electron has been promoted, the excited states are called (i) valence excited states if the virtual orbital is localized around the carbon atoms and contains numerous nodal surfaces, (ii) Rydberg states if the orbital is a diffuse hydrogenic orbital localized several tens of angstrom away from the fullerene cage or (iii) Super Atom Molecular Orbital (SAMO) states if the orbital has an hydrogenic character such as in Rydberg states but where the electronic density is localized inside or in the close vicinity of the fullerene cage. Therefore the SAMO states have binding energies that are a few eV higher than Rydberg states.

The SAMO states have been observed in STM experiments of fullerenes adsorbed on surfaces<sup>1-2</sup> and in photoelectron spectroscopy experiments of fullerenes such as  $\text{C}_{60}$ <sup>3-5</sup>,  $\text{C}_{70}$ ,  $\text{C}_{82}$ <sup>6</sup> or the endohedral fullerene  $\text{Sc}_3\text{N@C}_{80}$ .<sup>6</sup> Despite the dense manifold of excited states and the small number of SAMO states, in visible or near infrared femtosecond photoelectron spectroscopy experiments, the SAMO states dominate the photoelectron spectra because they ionize several orders of magnitude faster than the isoenergetic valence states. Due to the diffuse character and simple hydrogenic shape of the SAMOs, they ionize on a few femtosecond timescale while the valence states ionize on a longer picosecond timescale.<sup>7</sup> Therefore in experiments using femtosecond laser pulses only the SAMO states can ionize significantly during the pulse. The assignment of the SAMO states in the photoelectron spectra is confirmed by determining the angular distribution of the ionized electron<sup>3,7</sup> that directly depends on the patterns of the corresponding Dyson orbitals.<sup>8-10</sup> The Dyson orbital represents the orbital from which the electron is ionized and for the SAMO states, it corresponds to hydrogenic orbitals.

Before being ionized, the SAMO states need to be populated during the pulse and the photoexcitation mechanism strongly depends on the symmetry of the fullerenes. For  $\text{C}_{60}$  that has an icosahedral symmetry and belongs to the  $I_h$  point group, the SAMO states are not optically active and can only be accessed by vibronic coupling<sup>11</sup> between optically active valence states and the SAMO states, which can take several tens of femtosecond. However the high symmetry of the  $\text{C}_{60}$  fullerene can be broken by elongating the cage in one direction and doping the fullerene such as in the  $\text{Ho}_3\text{N@C}_{80}$  fullerene.<sup>12</sup> In endohedral fullerenes the degeneracy of the  $p$  and  $d$  SAMO is lifted and the SAMOs become optically active, which results in a higher ion yield for  $\text{Ho}_3\text{N@C}_{80}$  compared to  $\text{C}_{60}$  when ionized by a 800nm 30fs pulse at intensities lower than  $10^{14} \text{ W/cm}^2$ .<sup>12</sup> In this article we show that the optical activity and binding energy of the SAMO states of the endohedral  $\text{Li@C}_{60}^+$  fullerene strongly depends on the position of the lithium atom inside the  $\text{C}_{60}$  cage. This dependence should be reflected in the photoelectron spectrum and in the ion yield dependence with the laser intensity.

## 2. RESULTS

The optical properties and fragmentation of the neutral  $\text{Li@C}_{60}$  fullerene have been reported by the Campbell group.<sup>13-14</sup> In this proceeding, we focus on the optical activity of the SAMO states of the cationic close shell endohedral fullerene  $\text{Li@C}_{60}^+$ .<sup>15-16</sup> We first determined the equilibrium geometry of several  $\text{Li@C}_{60}^+$  conformers with the aim to determine the lowest energy one. The electronic structure computations are carried out at the DFT level with the B3LYP functional and a 6-31G(d) basis set for the carbon atoms and a 6-311++G(2df,3dp) basis set for the Li atom. The equilibrium geometries of the low energy conformers are shown in Fig. 1. The conformer with the  $\text{Li}^+$  atom centered in the cage (conformer 3 in Fig. 1) is the least stable.<sup>17</sup> There are three conformers within 0.5kcal/mol in which the  $\text{Li}^+$  atom is slightly off-center.

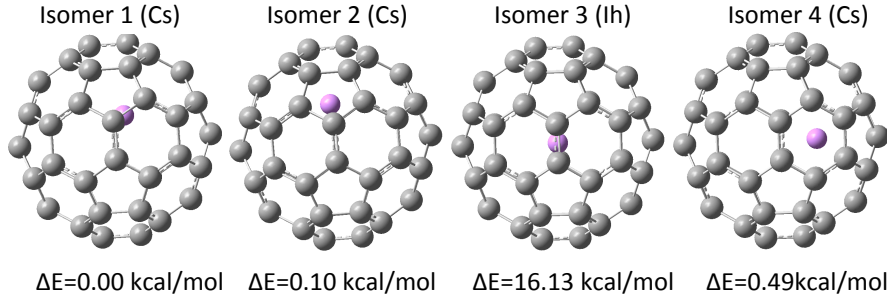


Fig. 1:  $\text{Li@C}_{60}^+$  conformers. The point group of each conformer and the energy difference with respect to the most stable conformer are also reported. In the isomer 1, 2 and 4, the lithium is off-center and localized respectively along a 6:5 bond (between a hexagon and pentagon), at the center of a pentagon and at the center of a hexagon for the projection of the fullerene shown here. The shortest Li-C bond for these three isomers is around 2.23 Å, which is shorter than the Li-C bond of the spherical isomer (3.53 Å).

We investigated the electronic structure of the SAMO states and Dyson orbitals for two of the four conformers (Fig. 2), the conformer 3 that retains the spherical symmetry of the bare  $\text{C}_{60}$  (the Li ion is at the center of the cage) and the lowest energy conformer in which the Li atom is off-center (conformer 1). The calculated ionization energies of the two conformers are respectively, 11.11eV and 11.02eV.

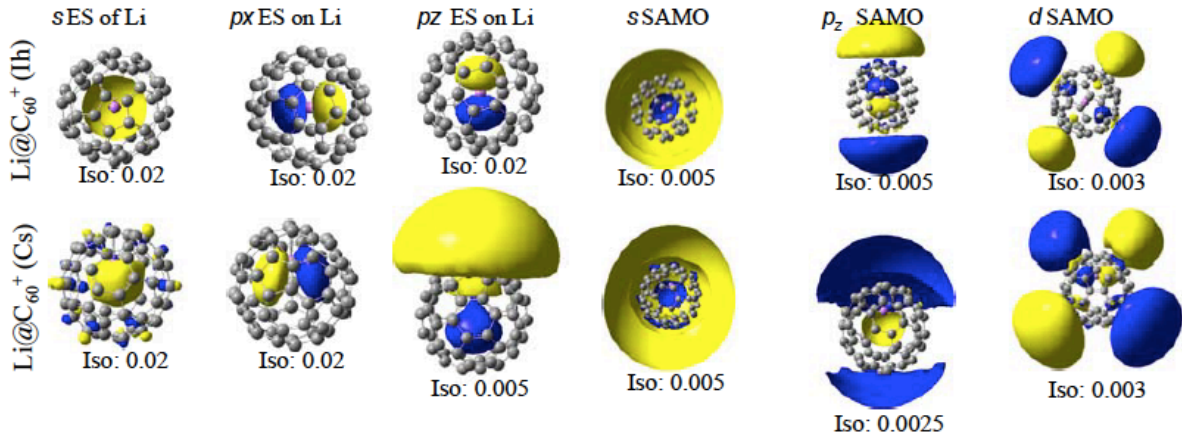


Fig. 2: Dyson orbitals of the excited states (ES) of the Li ion and the lowest band of  $\text{Li@C}_{60}^+$ 's SAMO states for the conformer 3 (Li center - Ih symmetry) and conformer 1 (Li off-center - Cs symmetry). The isocontours are expressed in  $|e|/\text{\AA}^3$ .

For the conformer 3 with the Li at the center of the cage, we computed the electronic structure of the 400 lowest excited states in CAM-B3LYP with the 6-31G(d) basis set for the C and a 6-31G(d)+6 *s,p,d* diffuse functions for the Li atom. In order to readily compute the electronic structure, we limited the excitations to build the excited states from the HOMO-4 to the LUMO+100.<sup>18</sup> Unlike in  $\text{C}_{60}$  the HOMO

is not five fold degenerate because of the endohedral Li ion. The energies of the SAMO and Rydberg states computed in the band of the 400 lowest excited states are reported in Table 1 and some of the Dyson orbitals are reported in Fig. 2. Amongst the excited states in which an electron has been excited to a hydrogen like orbital, we differentiate the excited states of the Li ion with respect to the SAMO states. The  $s$  and  $p$  excited states of the Li ion have a binding energy of respectively 7.22eV and 5.11eV and their Dyson orbitals are fully localized inside the fullerene cage. The SAMO states have smaller binding energies (Table 1) and their Dyson orbitals are localized both inside and in the close vicinity of the  $C_{60}$  cage. The first band of  $s$  and  $p$  SAMO (Fig. 2) are similar to one observed in the bare  $C_{60}$  except that the binding energies are larger, which can be understood from the positive charge of the endohedral fullerene.

Table 1: Binding energies (in eV) and magnitude of the transition dipole moment (in a.u.) between the ground state and the SAMO and Rydberg states of the endohedral fullerene  $Li@C_{60}^+$ .

	Conformer 3 (Ih - center)			Conformer 1 (Cs - off-center)		
		Binding energy	Dipole moment		Binding energy	Dipole moment
Li's excited states	$s$	7.76	0.00	$s$	6.71-6.84	0.03
	$p$	5.59-5.70	0.00	$p$	3.79-4.28	0.13
$C_{60}$ 's SAMO and Rydberg states	$s$ 1	3.72	0.00	$s$ 1	3.62	0.03
	$p$ 1	3.36-3.49	0.00	$p$ 1	3.58-3.83	0.06
	$d$ 1	3.03-3.27	0.13	$d$ 1	3.07-3.26	0.22
				$p$ 2	2.34-2.96	0.45
	$f$ 1	2.14-2.26	0.00	$f$ 1	2.03-2.63	0.13
	$s$ 2	2.14	0.00	$s$ 2	2.14	0.00
	$d$ 2	1.89	0.04	$d$ 2	1.81-1.90	0.10
				$p$ 3	1.75 - 1.83	0.02
	$s$ 3	1.57	0.00	$s$ 3	1.54	0.00
	$p$ 2	1.48	0.00	$p$ 4	1.30-1.43	0.05
	$g$ 1	1.36-1.51	0.14	$g$ 1	1.30-1.96	0.13
	$d$ 3	1.30	0.00			
	$p$ 3	1.14	0.00			
	$s$ 4	0.64	0.00			

For the lowest energy conformer, in which the Li ion is not localized at the center of the cage (conformer 1), we computed the electronic structure of the 400 lowest excited states using the same functional and basis set as for the centered  $Li@C_{60}^+$  except that we added a ghost atom localized at the center of cage with a 6-31G(d)+6  $s,p,d$  basis set in order to describe accurately SAMO and Rydberg states of the  $C_{60}$  cage. The change of position of the Li ion strongly affects the binding energies and Dyson orbitals of lithium excited states as well as of the  $p$  SAMO states (Table 1). The Dyson orbitals of the excited states in which an electron has been excited to  $s$  or  $p$  orbital of the Li ion exhibit a strong distortion compared to the Dyson orbitals of the spherical isomer (Fig. 2). The electronic density of the  $p_z$  component is localized both inside and outside the fullerene cage close to the Li ion. The  $s$  and  $d$  SAMO and Rydberg states are mostly left unaffected by the change of position of the Li ion and their binding energies are similar for both conformers (Table 1). It is not the case of the  $p$  SAMO states that are strongly distorted with an accumulation of electronic density on the  $p$  lobe close to the lithium ion, which impacts the binding energies. The  $f$  and  $g$  states have a broader range of binding energies due to the lifting of the degeneracy induced by the off-center Li ion. The bands of SAMO states are no longer well separated as is the case for  $s$  and  $p$  states in  $C_{60}$ . An interesting effect of the symmetry breaking induced by the off-center Li ion is the non-zero value of transition dipole moments between the ground state and the SAMO states. The magnitude of the transition dipole moments is significantly smaller than for the endohedral fullerene  $Ho_3N@C_{80}$  in which the large  $Ho_3N$  complex induces a stronger effect on the SAMO states than the Li ion. Unlike in the spherical  $C_{60}$  or  $Li@C_{60}^+$  with the Li centered in the cage, the SAMO states of  $Li@C_{60}^+$  with the lithium off-center can be optically accessed. The absorption spectrum should therefore strongly depend on the position of the Li atom in the cage.

#### 4. CONCLUSIONS

By using a time-saving way to compute the electronic structure of a large band of excited states in fullerenes in TDDFT, we were able to investigate the effect of the position of the lithium ion in  $\text{Li}@\text{C}_{60}^+$  conformers on the binding energies and transition dipole moments of SAMO states. When the lithium is localized at the center of the cage, the SAMO states are degenerate and they are not optically active, similar to the situation for  $\text{C}_{60}$ . Once the lithium is moved off-center, it breaks the spherical symmetry, which lifts the degeneracy of the SAMO states and makes them optically active.

#### 5. ACKNOWLEDGMENTS

We thank Olof Johansson, Elvira Bohl, Hui Xiong, Nora Berrah, Hui Li and Matthias Kling for involving us in the interpretation of their photoionization experiments on fullerenes. F.R. is a Director of Research and B.M. is a Postdoctoral Researcher with FNRS (Fonds National de la Recherche Scientifique), Belgium. This work is supported by the U.S. Department of Energy (DOE), Office of Science, Basic Energy Sciences (BES) under Award #DE-SC0012628. Computational resources have been provided by the Consortium des équipements de Calcul Intensif (CECI), funded by the Fonds de la Recherche Scientifique de Belgique (F.R.S.-FNRS) under Grant No. 2.5020.11.

#### REFERENCES

1. Feng, M.; Zhao, J.; Petek, H., Atomlike, Hollow-Core-Bound Molecular Orbitals of  $\text{C}_{60}$ . *Science* **2008**, *320* (5874), 359-362.
2. Feng, M.; Zhao, J.; Huang, T.; Zhu, X.; Petek, H., The Electronic Properties of Superatom States of Hollow Molecules. *Accounts of Chemical Research* **2011**, *44* (5), 360-368.
3. Johansson, J. O.; Henderson, G. G.; Remacle, F.; Campbell, E. E. B., Angular-resolved Photoelectron Spectroscopy of Superatom Orbitals of Fullerenes. *Physical Review Letters* **2012**, *108* (17), 173401.
4. Bohl, E.; Sokół, K. P.; Mignolet, B.; Thompson, J. O. F.; Johansson, J. O.; Remacle, F.; Campbell, E. E. B., Relative Photoionization Cross Sections of Super-Atom Molecular Orbitals (SAMOs) in  $\text{C}_{60}$ . *The Journal of Physical Chemistry A* **2015**, *119* (47), 11504-11508.
5. Li, H.; Mignolet, B.; Wang, Z.; Betsch, K. J.; Carnes, K. D.; Ben-Itzhak, I.; Cocke, C. L.; Remacle, F.; Kling, M. F., Transition from SAMO to Rydberg State Ionization in  $\text{C}_{60}$  in Femtosecond Laser Fields. *The Journal of Physical Chemistry Letters* **2016**, *7* (22), 4677-4682.
6. Olof Johansson, J.; Bohl, E.; Henderson, G. G.; Mignolet, B.; Dennis, T. J. S.; Remacle, F.; Campbell, E. E. B., Hot electron production and diffuse excited states in  $\text{C}_{70}$ ,  $\text{C}_{82}$ , and  $\text{Sc}_3\text{N}@\text{C}_{80}$  characterized by angular-resolved photoelectron spectroscopy. *The Journal of Chemical Physics* **2013**, *139* (8), 084309.
7. Mignolet, B.; Johansson, J. O.; Campbell, E. E. B.; Remacle, F., Probing Rapidly-Ionizing Super-Atom Molecular Orbitals in  $\text{C}_{60}$ : A Computational and Femtosecond Photoelectron Spectroscopy Study. *ChemPhysChem* **2013**, *14* (14), 3332-3340.
8. McWeeny, R.; Sutcliffe, B. T., *Methods of Molecular Quantum Mechanics*. Academic Press: London, 1969; Vol. 2.
9. Melania Oana, C.; Krylov, A. I., Dyson orbitals for ionization from the ground and electronically excited states within equation-of-motion coupled-cluster formalism: Theory, implementation, and examples. *The Journal of Chemical Physics* **2007**, *127* (23), 234106.
10. Mignolet, B.; Kùs, T.; Remacle, F., Imaging Orbitals by Ionization or Electron Attachment: The Role of Dyson Orbitals. In *Imaging and Manipulating Molecular Orbitals*, Grill, L.; Joachim, C., Eds. Springer Berlin Heidelberg: **2013**; pp 41-54.
11. Johansson, J. O.; Campbell, E. E. B., Probing excited electronic states and ionisation mechanisms of fullerenes. *Chemical Society Reviews* **2013**, *42* (13), 5661-5671.
12. Xiong, H.; Mignolet, B.; Fang, L.; Osipov, T.; Wolf, T. J. A.; Sistrunk, E.; Gühr, M.; Remacle, F.; Berrah, N., The Role of Super-Atom Molecular Orbitals in Doped Fullerenes in a Femtosecond Intense Laser Field. *Scientific Reports* **2017**, *7* (1), 121.
13. Gromov, A.; Ostrovskii, D.; Lassesson, A.; Jönsson, M.; Campbell, E. E. B., Fourier Transform Infrared and Raman Spectroscopic Study of Chromatographically Isolated  $\text{Li}@\text{C}_{60}$  and  $\text{Li}@\text{C}_{70}$ . *The Journal of Physical Chemistry B* **2003**, *107* (41), 11290-11301.
14. Lassesson, A.; Hansen, K.; Jönsson, M.; Gromov, A.; Campbell, E. E. B.; Boyle, M.; Pop, D.; Schulz, C. P.; Hertel, I. V.; Taninaka, A., A femtosecond laser study of the endohedral fullerenes  $\text{Li}@\text{C}_{60}$  and  $\text{La}@\text{C}_{82}$ . *The European Physical Journal D-Atomic, Molecular, Optical and Plasma Physics* **2005**, *34* (1-3), 205-209.
15. Okada, H.; Komuro, T.; Sakai, T.; Matsuo, Y.; Ono, Y.; Omote, K.; Yokoo, K.; Kawachi, K.; Kasama, Y.; Ono, S.; Hatakeyama, R.; Kaneko, T.; Tobita, H., Preparation of endohedral fullerene containing lithium ( $\text{Li}@\text{C}_{60}$ ) and isolation as pure hexafluorophosphate salt ( $[\text{Li}^+@\text{C}_{60}][\text{PF}_6^-]$ ). *RSC Advances* **2012**, *2* (28), 10624-10631.

16. Aoyagi, S.; Nishibori, E.; Sawa, H.; Sugimoto, K.; Takata, M.; Miyata, Y.; Kitaura, R.; Shinohara, H.; Okada, H.; Sakai, T.; Ono, Y.; Kawachi, K.; Yokoo, K.; Ono, S.; Omote, K.; Kasama, Y.; Ishikawa, S.; Komuro, T.; Tobita, H., A layered ionic crystal of polar Li@C<sub>60</sub> superatoms. *Nat Chem* **2010**, 2 (8), 678-683.
17. Slanina, Z.; Uhlik, F.; Lee, S.-L.; Adamowicz, L.; Nagase, S., Li<sub>x</sub>@C<sub>60</sub>: Calculations of the Encapsulation Energetics and Thermodynamics. *International journal of molecular sciences* **2008**, 9 (9), 1841-1850.
18. Mignolet, B.; Remacle, F., Time-efficient computation of the electronic structure of the C<sub>60</sub> super-atom molecular orbital (SAMO) states in TDDFT. *AIP Conference Proceedings* **2016**, 1790 (1), 020015.